AD-A230 014

spire

A Final Report for:

MOCVD OF LEAD-GERMANATE FOR NON-VOLATILE RAMs

Submitted under:

Contract Number: N00014-90-C-0127

SBIR, Phase I

1990

Principal Investigator:

Dr. Anton Carl Greenwald

Submitted to:

OFFICE OF NAVAL RESEARCH

Arlington, VA 22217-5000

Submitted by:

SPIRE CORPORATION

Patriots Park

Bedford, MA 01730

TABLE OF CONTENTS

DTIC
COPY
INSPECTED
6

A-1

LIST OF FIGURES

INTRODUCTION

The goal of this research is to fabricate thin film ferroelectric materials for use in non-volatile random access memory (NVRAMs) chips that are radiation resistant and can be used to replace existing memories with the same function in current Navy systems at great savings in weight and power requirements. Suitable non-volatile memories have been demonstrated using ferroelectric materials to store the information in binary code as the direction of polarization of the dielectric. However, these memories have not yet demonstrated adequate retention or cycle lifetime (fatigue) to be used in practical applications. Research is progressing to identify the flaws in existing technology and to explore alternate materials and fabrication methods to extend the fatigue of NVRAMs.

Phase I technical objectives were (1) to deposit a thin film of lead-germanate (PGO) with the correct stoichiometry and low levels of contaminants by metalorganic chemical vapor deposition (MOCVD), and (2) to deposit a similar film on a metal substrate, fabricate a capacitor and measure electrical properties. MOCVD of lead germanate has never been reported prior to this innovative work.

We achieved objective (1), the fabrication of stoichiometric lead-germanate films, and fabricated the capacitors required for objective (2).

1.0 BACKGROUND

Lead germanate is a ferroelectric material with low coercive field and high critical temperature. It is potentially useful for non-volatile random access memories (NVRAMs)[1] and has been deposited by sputtering with preferential orientation.[2] The goal of this research was to show improved thin films for this application using an innovative deposition technique, metalorganic chemical vapor deposition (MOCVD).

MOCVD has been demonstrated for lead titanate,[3-10] lead zirconia titanate,[11] and bismuth titanate.[12] Deposition sources and parameters vary significantly between these publications. The research reported herein was performed at atmospheric pressure because, at the start of the program, Spire had modest success with lead zirconium titanium films.[13]

We could not find a complete phase diagram by investigating the chemistry of the lead-germanium-oxide system. Binary alloy phase diagrams for Pb-O, Ge-O and Pb-Ge were referenced by Massalski.[14] Lead forms a eutectic around 327.5°C with 0.07 atomic percent germanium. However, small amounts of oxygen have a significant effect in this system. Pure
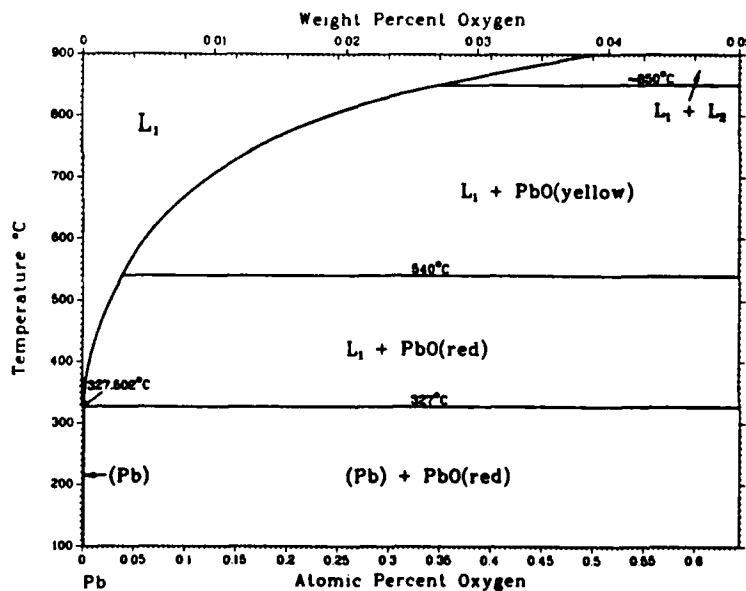

FIGURE 1. Pb - O BINARY PHASE DIAGRAM.

lead melts at the same temperature as given for the eutectic, but the addition of 0.5 atomic percent oxygen raises this melting temperature to over 900°C (Figure 1). Therefore, we do not expect the film to melt during deposition in the presence of any oxygen source.

The oxides of these materials will sublime. Germanium oxide, especially the mono-oxide, has a high vapor pressure; 10 torr at 680°C and 10^{-2} torr at 500°C.[15] Lead oxide has a lower vapor pressure, only 10^{-3} torr at 650°C. The vapor pressure of lead or germanium oxide over the compound lead-germanate (PGO) has not been reported. This data imply that the partial pressure of germanium compounds must be greater than the partial pressure of lead compounds in the MOCVD reactor for successful deposition of PGO. This is nct a problem as the vapor pressure of the source material for Ge is much larger than that for lead.

2.0 DEPOSITION FACILITIES

The apparatus used for this research is pictured in Figure 2. The gas control system is shown schematically in Figure 3. The system bubbles a carrier gas, either hydrogen or argon, through a liquid source. The carrier becomes saturated with vapor from the volatile liquid and is pushed into a heated reactor. The metalorganic compounds decompose when absorbed on a heated surface. A metal film can be deposited in the presence of excess hydrogen. In the presence of oxygen, an oxide film will be deposited due to chemical reactions on the surface of the heated substrate.

The complexity of the equipment in Figure 3 represents minimum requirements to control the mass flow of metalorganic species into the reactor to obtain the correct stoichiometry for $Pb_5Ge_3O_{11}$. The mass flow of metal species F_m is given by the equation:

$$F_m = F_c * P_b / (P_b - P_m)$$

FIGURE 2.   CHEMICAL VAPOR DEPOSITION REACTOR MODIFIED FOR
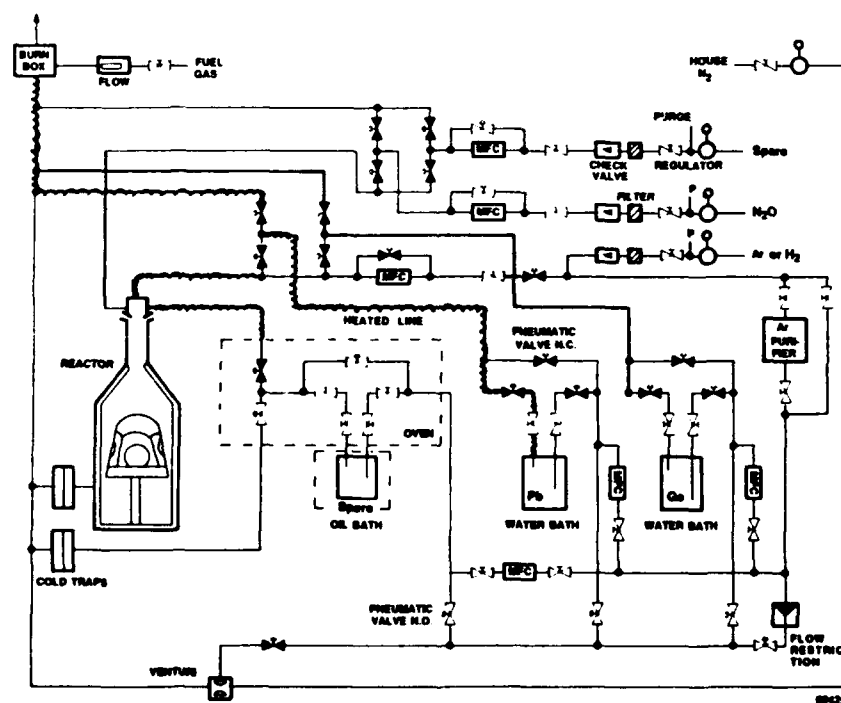   LEAD GERMANATE.

FIGURE 3. GAS CONTROL SYSTEM FOR MOCVD OF LEAD GERMANATE.

where F_c is the carrier flow through the bubbler at pressure P_b, and P_m is the vapor pressure of the metalorganic source. F_c is controlled by the mass flow controllers (MFCs) shown in Figure 3. The vapor pressure varies exponentially with temperature, Figure 4, and is controlled by maintaining the temperature of the source material to within $\pm0.01°C$.

The lead source chosen for use was tetra-ethyl lead, 99.9999% pure from Eagle Pitcher Laboratories. The germanium source was tetramethyl germanium, 99.999% pure available from CVD Inc., a division of Mortom Thiokol. Choice of source materials was based partially on concerns for safety, availability of high purity materials, and suitability for the proposed chemical reaction. There is no high pressure gaseous source for lead. GeH_4 is a high pressure gas source for germanium but requires a separate exhausted gas cabinet to handle the cylinder for toxic gases. This cabinet was not available, so a liquid source was chosen. Purity of the source materials was guaranteed by the vendors, analyses were provided.

The total amount of toxic material used in this process is very low; less than 500 cc's (less than one kilogram) per year of tetra-ethyl lead would suffice for production needs for all Navy systems. Even smaller amounts of germanium are required. Nevertheless, complete control of toxic materials is insured in two ways.

First, for normal operating conditions, all products exhausted from the reactor are collected and removed to proper waste disposal sites. Non-condensable vapors are burned and the resulting particulates are collected by a HEPA filter. Tests of exhausted air have been conducted to verify that no material is exhausted into the atmosphere. Condensable vapors are collected by a water-cooled trap. This trap, and the residue remaining in the reactor, are cleaned in a dedicated area where all waste is collected for proper removal.

Second, to prevent exposure of operating personnel to high levels of toxic vapors during an emergency (i.e., leak), all storage and reactor cabinets are vented by exhaust hoods. The leak is repaired by personnel wearing fully self-contained breathing apparatus.

- 4 -

Spire performs periodic checks of the apparatus for vapor leaks with extremely sensitive, chemical specific tests for tetra-ethyl lead. The germanium compound can be monitored continuously by other equipment set to detect silane. Additional tests for dust and deposits on surfaces of the laboratory are also performed. All personnel possibly exposed to hazardous material are given periodic physical exams and blood tests.

3.0 DEPOSITION OF SINGLE METAL OXIDES

Three types of substrates were used for deposition experiments. The simplest was a cleaned, bare silicon wafer typically 11 to 12 mils thick (uncut diameter was two inches). The second substrate was the same wafer with a 1000Å to 2000Å coating of sputtered platinum. The third type of substrate was a silicon wafer with a 1000Å thermal oxide grown on both surfaces. A 500Å titanium layer was then deposited, followed by 1500Å of platinum; all layers were deposited by sputtering. The <111> silicon wafers were purchased; all further processing was performed at Spire.

Transport of the metalorganic vapors to the reactor for deposition of oxides was not a problem. The vapor pressure of tetramethyl germanium is 139 torr at 0°C, while that of tetra-ethyl lead (0.1 torr at 17.8°C) is shown in Figure 4. Carrier flow rate for the lead compound had to be significantly greater than that for the germanium compound to make up the difference in vapor pressure.

The deposition rate of lead oxide was measured under a separate program.[13] For a fixed flow, Pb deposited at approximately 500Å to 1000Å per hour in argon with 40 to 400 ppma (parts per million, atomic %) nitrous oxide added for a substrate temperature in the range 300 to 500°C. The deposition rate fell off sharply at both higher and lower temperatures. At the low end, the compound was not reacting with the oxidant or decomposing without the oxidant. At the high temperature, lead oxide has a small but not insignificant vapor pressure and was evaporated off the surface of the sample.
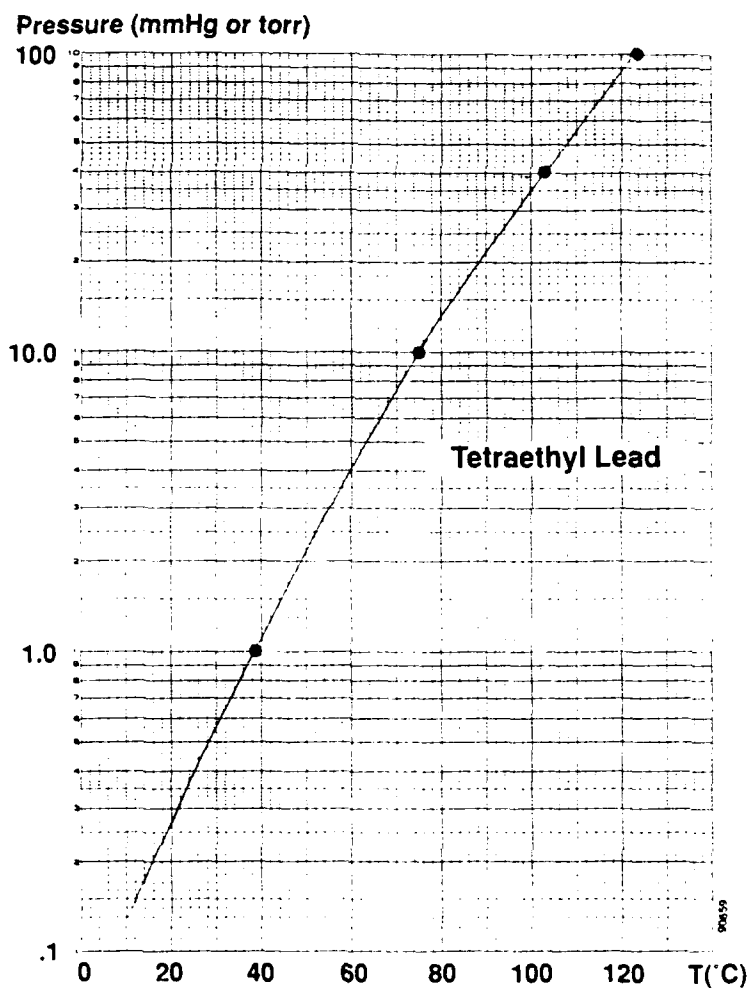
Pressure (mmHg or torr)

FIGURE 4. VAPOR PRESSURE OF TETRA-ETHYL LEAD (reference 11).

For this program, the deposition rate of lead was measured separately with pure hydrogen as a carrier gas. At 600°C, the deposition rate was 1000Å per hour, comparable to that observed with argon at lower temperatures. At 700°C, the deposition rate fell to 400Å per hour. There was no oxygen added to these test runs, but pure lead would easily melt at the given temperatures. This implies that there was sufficient residual oxygen during these tests to form an alloy that would not change state at elevated temperatures (Figure 1). The drop in deposition rate at 700°C could then be due to either too little oxygen to stabilize the matrix or to partial evaporation of the lead oxide formed.

The deposition rate of germanium oxide from the given source was measured in an argon and in an hydrogen atmosphere. Hydrogen suppressed the formation of oxygen and desorption of GeO, which is volatile. Measured film thickness after one hour deposition runs are plotted in Figure 5. The source, $Ge(CH_3)_4$, was held at $0^\circ C$; the carrier was argon at either 5 or 20 sccm; and remaining gas flow was 5 slpm of hydrogen. Reactor pressure was always atmospheric throughout this program, with a warm wall and a susceptor temperature as shown in Figure 5. If the dilution gas were changed to pure argon, the deposition fell to near zero. If the dilution gas were changed to argon and a sm ll amount of oxidant, such as N_2O, were added (40 to 400 ppma tested), the deposition rate increased to about one-third the value observed with hydrogen alone. In large concentrations of oxygen at atmospheric pressure, the deposition rate fell again. The linear relation of log (deposition rate) versus inverse temperature implies that the process is kinetically limited.
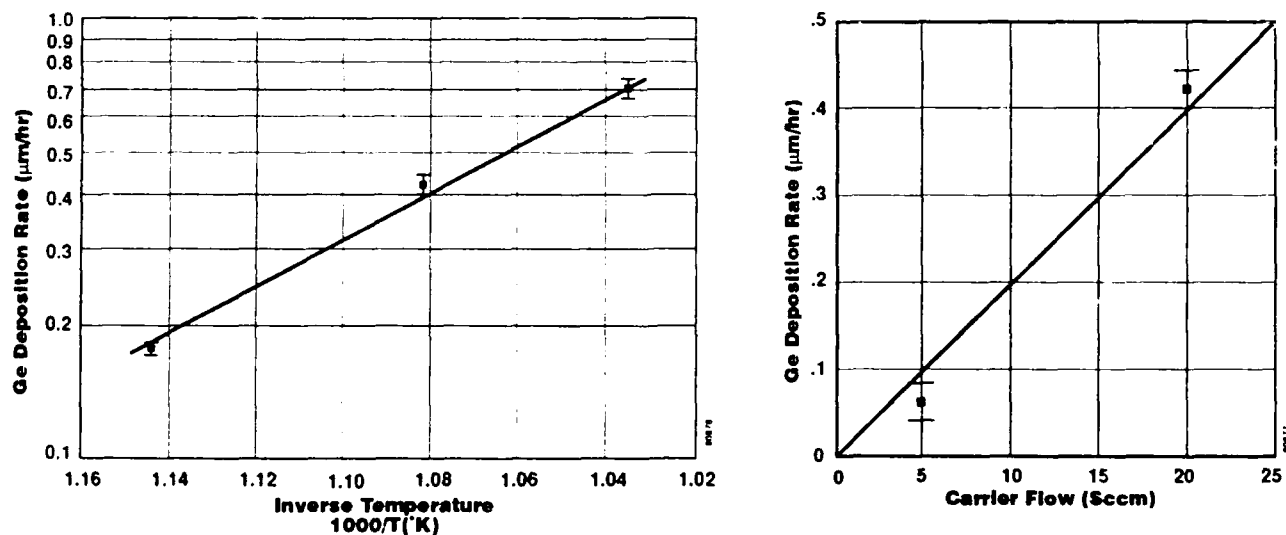

FIGURE 5.   DEPOSITION RATE OF GERMANIUM AND GERMANIUM OXIDE VERSUS TEMPERATURE AND CARRIER FLOW RATE.

4.0   DEPOSITION OF LEAD GERMANATE

Films containing both lead and germanium were deposited in hydrogen or argon atmospheres, with no oxidants and with low levels of nitrous oxide present, at temperatures varying from 400 to 650°C. Initial experiments used only argon as the carrier. The films were rough, with feature sizes comparable to the thickness of the film.

At 400°C, in argon with 400 ppma nitrous oxide added, there was no film deposited. At 500°C, there was a thick rough film with nearly the correct stoichiometry; 71% Pb and 29% Ge versus desired values of 62.5% and 37.5%, respectively. The film was highly conducting. After annealing at only 350°C for one hour, the composition changed, with the greatest loss of Ge: 81% Pb and only 19% Ge.

Combined lead and germanium films were deposited at 700°C in hydrogen. Continuous films of germanium (Figure 6), and continuous films of lead (Figure 7) were deposited in hydrogen. However, the combination of lead and germanium did not produce a continuous film (Figure 8). The composition was analyzed by Auger spectroscopy because measurements by EDS would be dominated by the signal from the substrate for such thin films. The result is shown in Figure 9. The substrate signal originates from areas between the germanium oxide grains. Titanium was seen, implying that the two underlying metals interdiffused at the deposition temperature. Lead was not seen. Our conclusion is that for these deposition conditions there was an interaction between the lead and germanium source chemicals or intermediates as they reacted on the sample surface to prevent deposition of lead. The interaction also seemed to affect nucleation density so that the film consists of separated crystals rather than a continuous film as in Figure 6. The experiment was repeated at lower temperature, 651°C. There was still no lead in the film.

The initial experiments with argon carrier gas were repeated with low levels of oxidant (40 ppma) added, at higher temperatures than before, up to 650°C. The deposited films were easily scratched and non-continuous (Figure 10). However, they did contain
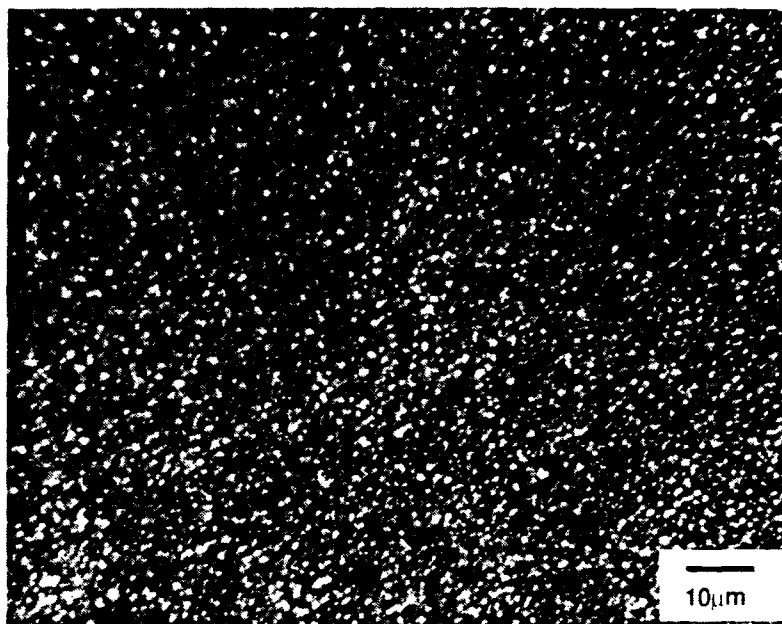
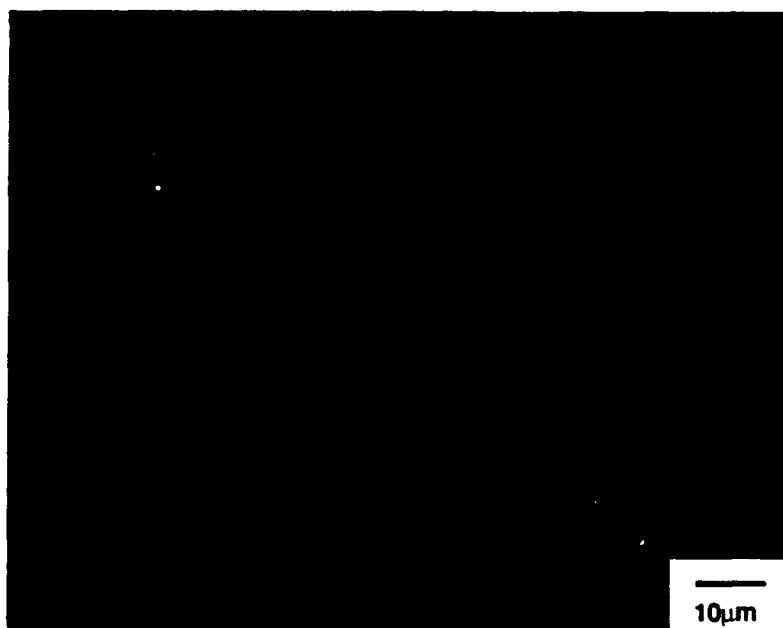FIGURE 6. LEAD - GERMANATE FILM DEPOSITED AT 700°C.
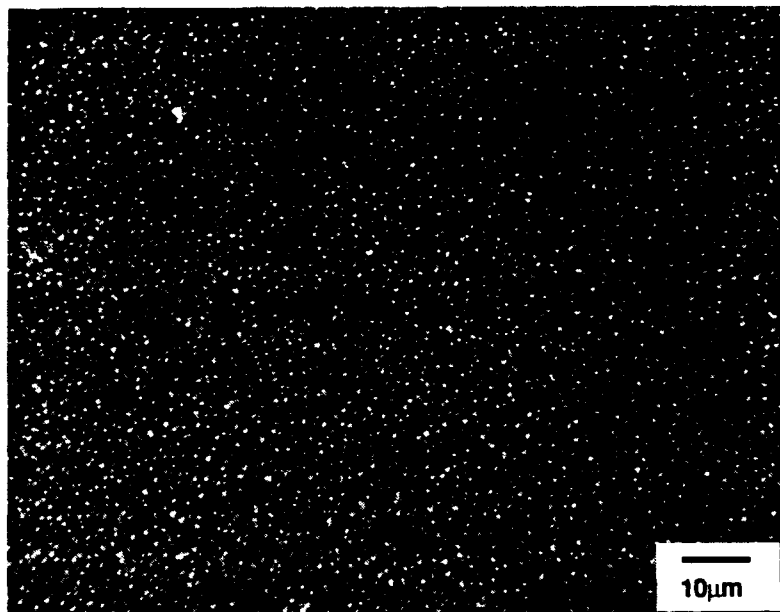

FIGURE 7. LEAD DEPOSITED ON Pt AT 700°C.
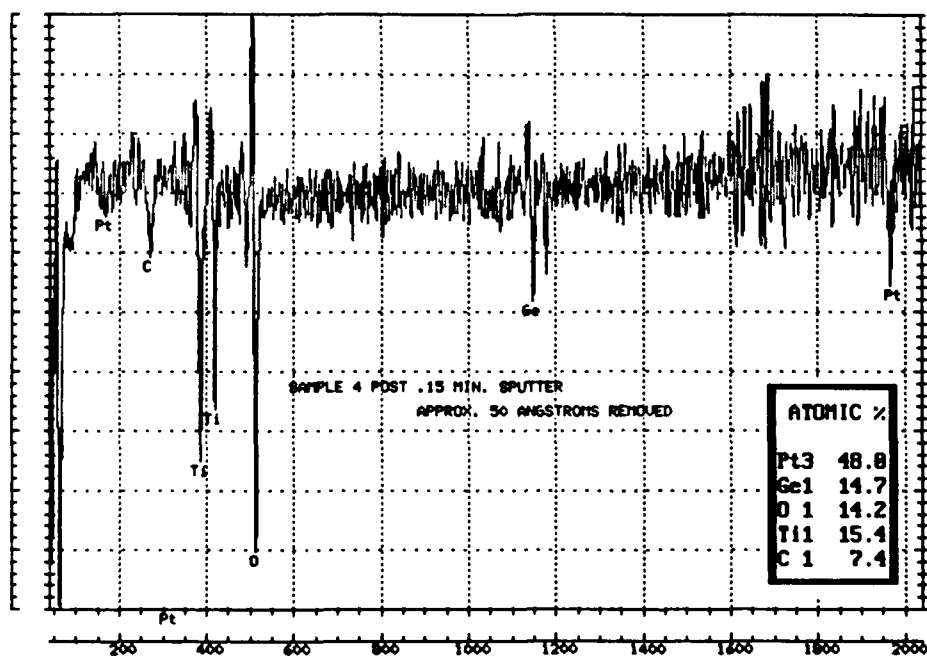
FIGURE 8. LEAD-GERMANATE FILM DEPOSITED AT /00°C.

FIGURE 9. AUGER SPECTROSCOPY SCAN OF THE SURFACE OF A Pt/Ti
COATED SUBSTRATE AFTER SIMULTANEOUS DEPOSITION OF
LEAD AND GERMANIUM.

- 10 -

appreciable amounts of lead; typical composition was 31% Pb, 69% Ge. Figure 11 is a typical EDS trace, showing that the signals for Pb and Ge could be distinguished without interference against a strong background from the substrate. The deposition rate was approximately 2500Å per hour. Not visible in Figure 10, were large crystals, over 2 microns diameter, that were widely scattered over the substrate.
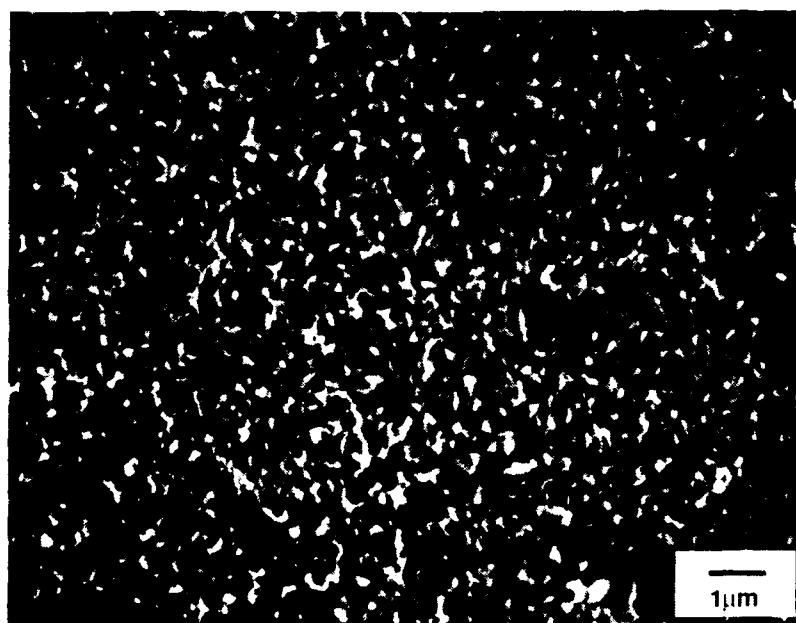

FIGURE 10.   LEAD GERMANATE FILMS DEPOSITED AT 650°C IN ARGON WITH N₂O ADDED.
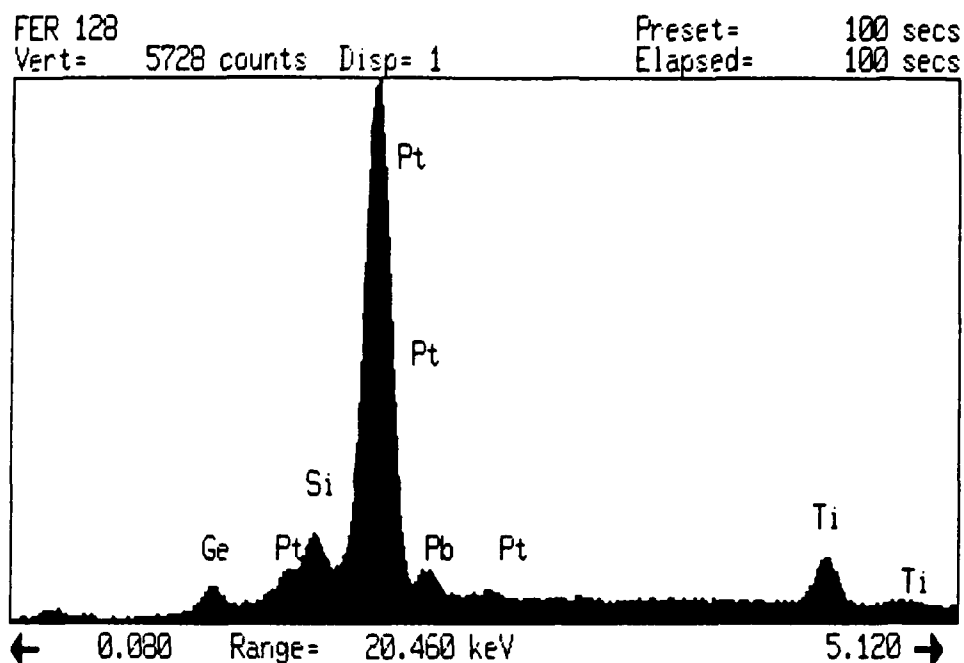
```
FER 128                              Preset=      100 secs
Vert=   5728 counts   Disp= 1        Elapsed=     100 secs
```

FIGURE 11. EDS SIGNAL FOR THE SAMPLE IN FIGURE 10.

5.0 SUMMARY

Spire deposited thin films of lead germanate by MOCVD on substrates typical of the materials now used to fabricate ferroelectric RAMs. The composition, ratio of Pb to Ge, could be easily controlled. More than 20 variables had to be optimized for MOCVD of lead-germanate. These include the source chemical, source temperature, source pressure, carrier gas, carrier flow, diluent and diluent flow for Pb and Ge as well as the reactor parameters of temperature, pressure, substrate surface, wall temperature, diluent, diluent flow, oxidant, oxidant flow, rates of heating and cooling. There are additional variables if post-deposition thermal treatment is considered. Spire completed 23 separate depositions, and succeeded in producing $Pb_5Ge_3O_4$.

Researchers using lead zirconia titanate have very recently published work implying that low pressure deposition could improve surface morphology and allow the use of higher concentrations of oxygen without gas phase nucleation.[11] Further development should follow this direction.

6.0 REFERENCES

1. S. B. Krupanidhi et al., Ferroelectrics, 50, 117 (1983).

2. H. Schmitt et al., Ferroelectrics, 56, 141 (1984).

3. T. Nakagawa et al., Jpn. J. Appl. Phys., 10, L655 (1982).

4. M. Okuyama and Y. Hamakawa, Ferroelectrics, 63, 243 (1985).

5. S.G. Yoon and H.G. Kim, J. Electrochem. Soc., 135, 3137 (1988).

6. S.L. Swartz et al., presented at the ISAF Conf., Zurich, (1988).

7. B.S. Kwak et al., Appl. Phys. Lett., 53, 1702 (1988).

8. M. Okada et al., Jpn. J. Appl. Phys., 28, 1030 (1989).

9. F.W. Ainger et al., presented at the Spring Meeting of the Materials Research Society, San Diego, 1990 (to be published).

10. S.G. Yoon and H.G. Kim, IEEE Trans. Ultrasonics, Ferroelectrics and Freq. Control, 37, 333 (1990).

11. M. Okada et al., Jpn. J. Appl. Phys., 29, 718 (1990).

12. L.A. Wills and B. Wessels, Northwestern University, presented at the 1990 Electronic Materials Conference, Santa Barbara, CA.

13. Subcontract to Charles Stark Draper Laboratory number 785.

14. T.B. Massalski, editor, Binary Alloy Phase Diagrams, (American Society for Metals, Metals Park, OH, 1986).

15. Balzers evaporation source catalog, 1989.